

The University of Chicago

THE ADDITION OF HALOGEN ACIDS TO UNSATURATED SUBSTANCES

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1939

By
CHEVES WALLING

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The Addition of Hydrogen Halides to *cis*- and *trans*-2-Pentene

Introduction

Over ten years have elapsed since Kharasch and Darkis² published their interpretation of the addition of hydrogen bromide to 2-pentene. At that time, and for some time thereafter, the results of various workers²⁻⁴ seemed to indicate different ratios of products depending upon the conditions of addition and the source and previous

treatment of the pentene employed. To account for this phenomenon, Kharasch and Darkis² postulated the existence of two isomeric 2-pentenes (electromers) differing in their electronic configurations, of which one added hydrogen bromide to give 2-bromopentane, and the other, 3-bromopentane.

More recently the matter has been investigated by Lauer and Stodola⁵ and Lucas and Prater.⁶ The latter authors isolated the *cis* and *trans* isomers of 2-pentene, and claim, on the

(2) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928).

(3) Lucas and Moyse, *J. Am. Chem. Soc.*, **47**, 1459 (1925); Lucas, Simpson, and Carter, *ibid.*, **47**, 1462 (1925).

(4) Sherrill, Otto, and Pickett, *ibid.*, **51**, 3023 (1929); Sherrill, Baldwin, and Haas, *ibid.*, **51**, 3034 (1929).

(5) Lauer and Stodola, *ibid.*, **56**, 1216 (1934).

(6) Lucas and Prater, *ibid.*, **59**, 1682 (1937).

TABLE I
 PHYSICAL CONSTANTS OF 2-PENTENES AND THEIR ADDITION PRODUCTS

Compound	This paper			Other workers			Ref.
	B. p., °C.	Pressure, mm.	n_D^{20}	B. p., °C.	Mm.	n_D^{20}	
2-Bromopentane	58.4-58.8	100	1.4412			1.4412	4
						1.4416	3
3-Bromopentane	59.0-59.5	100	1.4444			1.4443	4
						1.4443	3
2-Chloropentane	95.5-96.0	755	1.4068	96.84-86	760	1.4069	9
3-Chloropentane	96.8-97.2	755	1.4103	97.76-82	760	1.4104	9
<i>cis</i> -2-Pentene	36.5	755	1.3825		37.0	1.3822	8
					36.5	1.3817	7
					36.2	1.3817	6
<i>trans</i> -2-Pentene	36.0	755	1.3798		36.25	1.3790	8
	35.9	740	1.3798		36.2	1.3799	6
				35.7 -	.9	1.3797	5

basis of rather meager experimental evidence, that the two isomers add hydrogen bromide to give different proportions of 2- and 3-bromopentane.

It should be noted that, with the exception of Lauer and Stodola, all investigators have used the index of refraction to determine the composition of the reaction mixture, and have obtained a variety of results. Lauer and Stodola converted the mixture of bromides into anilides and found that their addition products contained approximately equal quantities of the two bromides.

To account for the lack of agreement between various groups of workers, and because of the far-reaching advances which have been made in recent years in our knowledge of the factors influencing the rate and direction of addition of hydrogen bromide to a large number of unsaturated compounds, a careful reinvestigation of the addition of hydrogen bromide and hydrogen chloride to both *cis*- and *trans*-2-pentene appeared desirable.

The present paper confirms the results of Lauer and Stodola on the addition of hydrogen bromide to *trans*-2-pentene. Furthermore, it shows that the addition of hydrogen chloride as well as hydrogen bromide to both *cis*- and *trans*-2-pentene results in an equimolecular mixture of 2- and 3-halopentanes regardless of the conditions of addition.

Preparation of 2-Pentene

Three methods of preparing 2-pentene were selected to give products of definite composition in sufficient amounts for study. 2-Pentene was prepared by the elimination of hydrogen bromide from (I) 2-bromopentane and (II) 3-bromopentane, and (III) by the partial hydrogenation of 3-pentyne. A fourth method, the treatment of a

carefully purified sample of one of the two isomeric 2,3-dibromopentanes with zinc, was investigated, but the amount of pentene obtained was too small to permit more than an investigation of its physical properties.

The pentenes from 2- and 3-bromopentanes were found, after repeated fractionations through a 1.5-m. column of both the pure hydrocarbons and their azeotropic mixtures with methyl alcohol, to be identical. Their physical constants show that both are either the *trans* modification^{5,6} or a mixture of *cis* and *trans* rich in the latter.⁷ The data support the view of Lucas and Prater⁶ that previous preparations⁴ differed in their content of 1-pentene.

The pentene from the partial hydrogenation of 2-pentyne had physical constants in good agreement with those recorded by Sherrill and Launsbach⁸ for a similar preparation. This, together with its manner of preparation, indicates it to be largely or entirely the *cis* isomer.⁷

The pentene from the higher-melting 2,3-dibromopentane had similar properties, so that it, too, is apparently the *cis* isomer.

The constants which have been obtained for the *cis*- and *trans*-2-pentenes and for the 2- and 3-halopentanes are summarized in Table I.

Experimental

2-Pentanol was prepared via the Grignard reagent from *n*-propyl bromide and acetaldehyde according to the directions of Wood and Scarf.¹⁰ The constants for the product were: n_D^{20} 1.4063-7; b. p. 117-118.5°.

2-Bromopentane was prepared by saturation of the alcohol with hydrogen bromide at 10° and warming to 60° on a

(7) Sherrill and Matlack, *J. Am. Chem. Soc.*, **59**, 2134 (1937).

(8) Sherrill and Launsbach, *ibid.*, **60**, 2562 (1938).

(9) Whitmore and Karnatz, *ibid.*, **60**, 2538 (1938).

(10) Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

water-bath. This process was repeated until no more hydrogen bromide was absorbed. A product was obtained in 90% yield upon working up in the usual manner; n_D^{20} 1.4412.

2-Pentene (method I) was prepared from 2-bromopentane by the method of Sherrill, Baldwin and Haas.⁴ After repeated fractionations of the azeotropic mixture with methyl alcohol (b. p. at 739 mm., 30.8–31.1°) through a 1.5-m. packed column, 2-pentene having the constants, b. p. (740 mm.) 35.9°, n_D^{20} 1.3798, was obtained in 32% yield.

3-Pentanol was obtained from two sources: (a) a sample of "synthetic diethyl carbinol" from the Eastman Kodak Company, b. p. 110–115°, n_D^{20} 1.4095–1.4106, and (b) a material obtained in 75% yield via the Grignard reaction between methyl formate and ethylmagnesium bromide, b. p. 114–114.5°.

3-Bromopentane was prepared in the same manner as its isomer, in yields of about 80%. The indices of products from three preparations varied between n_D^{20} 1.4443 and 1.4445. I have taken 1.4444 as being the probable index for the pure substance.

2-Pentene (method II) was prepared from 3-bromopentane in the same manner as from 2-bromopentane, and the yield of pure product on a representative preparation was 60%. The products, whether purified by distillation of their azeotropic mixtures (b. p. 749 mm., 31.0–31.1°) with methyl alcohol through a 1.5-m. packed column, or by distillation of the pure hydrocarbon alone through a Podbielniak column¹¹ were identical with each other and with pentene prepared by method I. Constants were b. p. (755 mm.) 36.0°, n_D^{20} 1.3798.

2-Pentyne (method III).—2-Pentyne was prepared from acetylene via ethylacetylene, as this seemed the most practical method for obtaining large quantities of the material.

Ethylacetylene was prepared from acetylene, sodium, and diethyl sulfate in liquid ammonia.¹² A specially constructed three-necked cylindrical flask with stirrer was used which fitted into a gallon (4-liter) dewar vessel. The latter was filled with an acetone–solid carbon dioxide mixture, as it was found that cooling both prevented loss of liquid ammonia and aided in controlling the reaction during the addition of diethyl sulfate. This last was added at such a rate that no product came off until the reaction was complete. The product was fractionated once through an 8-bulb column to remove acetylene, b. p. 10–20°. Yields as high as 172 g. (64%) were obtained from 5 moles of sodium.

2-Pentyne was prepared from the magnesium bromide derivative of ethylacetylene (prepared from ethylacetylene and ethylmagnesium bromide) and dimethyl sulfate.¹³ After the addition of dimethyl sulfate and before hydrolysis, the product and ether were removed from the reaction vessel by distillation. A further amount of product was obtained following the addition of water by collecting all material volatile at the temperature of a steam-bath.

The 2-pentyne was separated from ether by distillation through a 1.5-m. packed column, to give a fraction boiling 54.5–56.5°. Continued refractionation of this portion

through a Podbielniak column gave the pure acetylene, b. p. (755 mm.) 55.6–55.9°, n_D^{20} 1.4035. From 294 g., of ethylacetylene, 580 g. of ethyl bromide, 1500 g. of diethyl sulfate, and excess magnesium, 153 g. (41%) of pure 2-pentyne were obtained.

Preparation of 2-Pentene.—The 2-pentyne was hydrogenated at 0° and atmospheric pressure in methyl alcohol solution. The vessel employed was a 200-cc. flask fitted with inlet and outlet tubes for gas and a mercury seal stirrer. Eighteen grams of pentyne was treated at a time. The progress of the reaction, which was allowed to proceed until 0.7 to 0.9 mole of hydrogen per mole of pentyne had been absorbed, was followed by measuring the volume of hydrogen consumed. One to three hours were required for reaction, depending upon the effectiveness of stirring and the activity of the catalyst, 5% palladium on barium sulfate prepared according to Schmidt.¹⁴ The product was distilled from solution, washed with water to remove alcohol, dried over barium oxide, and distilled through a Podbielniak column. A fraction boiling over not more than 0.4° was collected, the yields approximating 50%. The index of refraction of the pure pentene was n_D^{20} 1.3823–5.

Occasional hydrogenations, particularly with new catalyst, gave products with a lower index (approximately n_D^{20} 1.3810). I have no adequate explanation to advance for this phenomenon, but such products were not used in the addition experiments.

2-Pentene from 2,3-Dibromopentane.—Samples of *cis*-2-pentene of low refractive index (as indicated just above) were combined and brominated at –78° in the absence of a solvent. After washing with cold, concentrated sulfuric acid and distilling, 121 g. of dibromide was obtained, which was then crystallized repeatedly from 90–98% aqueous methanol at –78°. After six recrystallizations, the melting point became constant at –33°. Thirty-three grams of this pure dibromopentane was treated with zinc in ethyl alcohol and the resulting pentene (6.7 g.) was distilled through a Podbielniak column. The fraction of b. p. (750 mm.) 36.0–36.4° had an index n_D^{20} 1.3825, indicating it to be pure *cis*-2-pentene.

Addition of Hydrogen Bromide and Hydrogen Chloride and Analysis of Addition Products.—

Hydrogen bromide was added to the pentenes from three sources under a variety of conditions as indicated in Table II. The index of refraction of the products varied between n_D^{20} 1.4429 and 1.4434, corresponding to a product containing 52–69% 3-bromopentane. As this whole range in index is covered by the addition products to the pentene of source II with which most of the experiments were made, and as the nine additions in acetic acid cover almost as large a range (n_D^{20} 1.4429–33), it appears that the ratio of addition products is independent of both the isomer of 2-pentene employed and the conditions of addition.

As all the determinations of the proportions of the two bromides had been made by index of re-

(11) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

(12) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

(13) Thorn, Hennion and Nieuwland, *J. Am. Chem. Soc.*, **58**, 796 (1936).

(14) E. Schmidt, *Ber.*, **52**, 409 (1919).

TABLE II
 THE ADDITION OF HYDROGEN BROMIDE TO 2-PENTENE

Source of pentene ^a	Moles HBr ^b	Substance added	Moles ^b	Reaction Time, hours	Temp., °C.	Method of isolation ^c	Yield, %	n_D^{20} ^d	Remarks
I	1.8	Acetic acid	3.6	2	0	1	90	1.4431	
				40	20				
II	1.8	Acetic acid	3.6	2	0				
				40	20	1	90	1.4431	
II	1.8	Acetic acid	3.6	2	5	1	80	1.4433	Pentene heated and illuminated in xylene (24 hrs.)
I	1.7	Acetic acid	1.5	2	0	1	74	1.4431	
II	1.8	Acetic acid	4.2	0.5	20	2	60	1.4429	
III	2.0	Acetic acid	4.0	48	20	2	..	1.4431	
III	2.0	Acetic acid	2	12	20	2	70	1.4431	
III	1.6	Acetic acid	2	0.75	20	1	85	1.4429	15 g. pentene used ^e
						2		1.4429	
II	1.6	Acetic acid	2	0.75	20	1	85	1.4429	15 g. pentene used ^e
						2		1.4430	
III	1.7	Diphenylamine	0.04	1	78	2	60	1.4430	Vacuum
I	1.5	Thiophenol	.03	1	80	1	88	1.4433	Vacuum
				20	5				
II	1.5	Thiophenol	.03	1	80	1	88	1.4432	Vacuum
				20	5				
II	1.5	Thiophenol	.03	1	80	1	75	1.4433	Vacuum
				20	5				
II	1.5	Thiocresol	.04	1	80	1	82	1.4433	Vacuum
				20	5				
I	1.5	None		2	75	1	65	1.4434	Some polymerization
				1	0				
II	1.3	FeBr ₃	.005	2	78	2	50	1.4430	
III	1.3	FeBr ₃	.005	2	78	2	60	1.4429	
III	1.2	Ascaridole	.05	0.75	0	2	..	1.4430	
II	1.5	Benzoyl peroxide	.01	2	0	1	36	1.4434	

^a Numeral indicates source of pentene. Sources I and II yield *trans*-2-pentene; source III, *cis*-2-pentene. ^b Expressed in moles per mole of pentene. ^c (1) Product vacuum distilled (100 mm.), all volatile products which condensed at room temperature collected. (2) Product distilled through 40-cm. column at atmospheric pressure, 1° fraction collected. ^d n_D^{20} 1.4428 corresponds to a mixture of equal proportions of 2- and 3-bromopentane. An increase of 0.0001 corresponds to an increase of 3% in the proportion of 3-bromopentane. ^e A portion of product isolated by each method, remainder fractionated (see experimental part).

fraction measurements, and as this method is inaccurate if a third substance is present, it seemed advisable to prepare larger quantities of the mixed bromides from both *cis*- and *trans*-2-pentene and to submit these to a careful fractionation which might be presumed to remove all impurities of higher and lower boiling point than the 2- and 3-bromopentanes. The mid-fractions from this purification were then analyzed both by index of refraction and by the mixed anilide method of Lauer and Stodola,⁵ using their melting point curves. Both results agreed within the limit of error (3%) and indicated an equimolar mixture of 2- and 3-bromopentanes for the entire addition product. From these data, given in detail in the experimental part, I conclude that analysis by index of refraction, as ordinarily employed, gives results which indicate the propor-

tion of 3-bromopentane to be too high by 2-28%.

Hydrogen chloride was added to the isomers of 2-pentene in the presence of acetic acid as solvent or ferric chloride as catalyst. The results are given in Table III. In order to obtain constant indices of refraction, it was found necessary to fractionate the products through a Podbielniak column. They were then analyzed both by index of refraction and by the melting points of their anilide derivatives. Neither method gives results differing from an equimolar mixture of 2- and 3-chloropentane by more than the probable experimental error; but, due to the difficulty in obtaining reproducible indices, the anilide method is believed to be the more reliable.

Experimental

Addition of hydrogen bromide was carried out as indicated in Table II, 5 g. of pentene usually being employed.

TABLE III
 ADDITION OF HCl TO 2-PENTENE

Run	Pentene ^a	Moles ^b HCl	Substance added	Moles ^b	Time, hours	Reaction Temp., °C.	n_D^{20} ^c	M. p. of anilide, °C.	3%-chloro- pentane
1 ^d	II	2.0	FeCl ₃	0.005	12	20	1.4082	84.1	45-48%
2 ^e	III	2.0	FeCl ₃	.005	12	20	1.4081		
3	II	2.2	FeCl ₃	.005	12	20	1.4082		
4	III	2.2	FeCl ₃	.005	12	20	1.4081		
5	II	1.2	Acetic acid	2	96	20	1.4082	84.1	45-48%
6	III	1.2	Acetic acid	2	96	20	1.4083	83.3	47%

^{a, b} Have the same significance as in Table II. ^c Taking the index of refraction as a linear function of composition 1.4081, 1.4082, and 1.4083 correspond, respectively, to 37, 40, and 43% of 3-chloropentane. ^d As two experiments on *trans*-pentene fractionated on a short column failed to give reproducible indices, they were combined to make (1), fractionated on a Podbielniak column and analyzed. ^e Same as *d* for two experiments of *cis*-pentene.

In the cases marked "vacuum" the usual vacuum technique developed in this Laboratory was used.¹⁵ All products were washed successively with cold, concd. sulfuric acid, water, and sodium carbonate solution, and dried over either calcium chloride or potassium carbonate.

Two methods of distilling the products were used, as explained in Table II. Due to the elimination of some high- and low-boiling fractions, yields by method (2) were lower than by method (1) (40-60%), and it will also be noted that the average index by this method is nearer to what is considered to be the most probable value, 1.4428, that of an equimolecular mixture.

In order to investigate this difference and to determine as accurately as possible the actual ratio of the two bromides, 15-g. samples of both *cis*- and *trans*-2-pentene were treated with hydrogen bromide in acetic acid, and the product washed and dried in the usual manner. A yield of 85% was obtained before distillation.

Five grams of each product was now distilled by methods (1) and (2) and analyzed by index of refraction. Results are indicated in Table II. The remaining portions of the addition products were now carefully fractionated through a Podbielniak column with the results shown in Table IV. The small spread in indices indicates that no appreciable error is introduced into the determination by neglecting the first and last fractions. The mean index of fractions II-V corresponds in each case to a mixture containing 50-52% 3-bromopentane.

 TABLE IV
 FRACTIONATION OF HYDROGEN BROMIDE ADDITION PRODUCTS OF 2-PENTENE

Fraction	<i>Trans</i>		<i>Cis</i>	
	Wt., g.	n_D^{20}	Wt., g.	n_D^{20}
I	1.0	1.4425	1.1	1.4425
II	1.7	1.4427-8	1.9	1.4427-8
III	3.5	1.4428	4.0	1.4428
IV	3.3	1.4429	3.2	1.4429
V	2.4	1.4430	1.8	1.4430
VI	0.8	1.4434	1.0	1.4432
VII ^a	2.3	..	3.0	..

^a VII.—Mechanical loss and non-volatile material.

A portion of the combined fractions II-V of each addition product was converted to the mixed anilide derivative

(15) Kharasch and Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933). For several years the vacuum employed in such work has been 10^{-4} to 10^{-5} mm. rather than 1 mm. as indicated in this paper.

by the method of Lauer and Stodola. Using their melting point curve, the m. p. of the anilides (94.3-4.4°) corresponds to a mixture containing 50-51% 3-bromopentane.

Addition of hydrogen chloride was carried out by two methods: (a) the pentene (5-7 g.) to which 0.2 g. of ferric chloride had been added, was placed in a Pyrex bomb-tube and cooled in liquid nitrogen. Hydrogen chloride (7-10 g. depending upon the amount of pentene used) was then passed in and the tube sealed. After one-half hour at -80° and four to twelve hours at 20°, the tube was again cooled and opened. The product was washed and dried in the same manner as the hydrogen bromide addition products and fractionated through a Podbielniak column.

(b) A mixture of 5 g. of pentene and 10 cc. of acetic acid was cooled to -80° in a Pyrex bomb-tube and saturated with about 3.5 g. of hydrogen chloride. The tube was sealed and allowed to stand at room temperature for four days. It was then cooled to -80°, opened, and the product washed and distilled as above.

In order to investigate further the composition of the mixed chlorides, the products of runs 1-4 were combined and refractionated through the same column. The index of the middle two-thirds, cut into three fractions, varied from n_D^{20} 1.4082 to 1.4084. The mean value (1.4083) corresponds to a mixture containing 44% 3-chloropentane.

To check the results obtained above, two portions of the mid-fraction above were converted to their anilides, as were portions of experiments 5 and 6. Since the melting point curve of Lauer and Stodola indicates the melting points of anilides from known mixtures of 2- and 3-bromopentanes, it was necessary to construct a new curve for anilides prepared from known mixtures of the pure 2- and 3-chloropentanes. This curve, while similar to theirs, is shifted to one side (Fig. 1) and was used in all the analyses of the hydrogen chloride addition products. Unfortunately, the melting points of the anilides from the mixed chlorides lie so near the eutectic point of the curve that a greater error is introduced than in the case of the bromides.

Preparation of Pure Halides.—Pure samples of 2- and 3-bromopentane were prepared as already described and were distilled to constant index through a Podbielniak column (Table I).

Pure chloropentanes were prepared according to Whitmore and Karnatz⁹ and similarly purified by distillation. The constants are in good agreement with theirs (Table I).

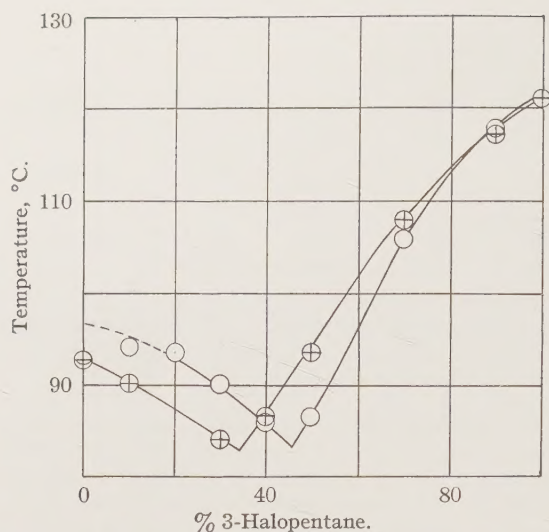


Fig. 1.—Melting points of anilides from mixtures of 2- and 3-halopentanes: $\oplus$ — $\oplus$, bromopentanes (Lauer and Stodola); $\circ$ — $\circ$, chloropentanes (this paper).

Discussion

Several years ago Kharasch and Reinmuth pointed out that the cases where two products were to be expected in the (normal) addition of halogen acids to an ethylenic bond were those where the ethylene was symmetrically substituted by groups of about equal electronegativity.¹⁶ Essentially the same rule recently has been advanced by Smith¹⁷ for hydrocarbons of the type $\text{CH}_3-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{CH}_2\text{R}$. At that time 2-pentene furnished the only instance of addition to a double bond to give two products, except for those in which a peroxide effect has since been shown to be involved. However, several compounds have since been shown clearly to give rise to two products upon normal addition of halogen acids: Δ^9 -undecenoic acid,¹⁸ Δ^9 -undecenol-1,¹⁸ Δ^2 -pentenoic acid,¹⁹ 1-bromopropene,²⁰ and *p*-chlorostilbene.²¹ It is to be noted that all the above compounds are ethylenes symmetrically substituted with radicals of similar electronegativity. The possible exception is 1-bromopropene; here one of the substituents is bromine and halogens do not seem to fall within their classification of electronegativity.²²

(16) Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).

(17) J. C. Smith, *Chemistry and Industry*, **15**, 833 (1937).

(18) Abraham, Mowat and Smith, *J. Chem. Soc.*, 948 (1937).

(19) Boorman, Linstead and Rydon, *ibid.*, 568 (1933).

(20) Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(21) Bloodgood, Ph.D. dissertation, The University of Chicago, 1931.

(22) Kharasch and Flenner, *J. Am. Chem. Soc.*, **54**, 674 (1932).

Recently Kharasch, Engelmann, and Mayo²⁰ discussed the significance of the formation of two products by normal addition of halogen acids and it was pointed out that this phenomenon might arise in either of two ways: (1) the ethylene may exist in two forms, each giving rise to only one product; (2) the ethylene may exist in only one form. The double bond, however, is so slightly polar that the activation energies for the alternative reactions are very nearly the same.

The first alternative, that the ethylene may exist in two forms, admits of two possibilities: (a) the two forms differ in atomic configuration; (b) the two forms differ in electronic configuration. For ethylenic compounds of the type investigated, only one type of isomerism involving atomic configuration has ever been demonstrated: *cis-trans* isomerism. In all cases investigated (1-bromopropene²⁰ and 2-pentene), both geometrical isomers have been shown to give identical mixtures of products. The second type of isomerism, namely, differences in electronic configuration, it appears can now be dismissed. Not only is conclusive chemical evidence for such isomerism lacking, but the point of view of present-day physics leads to the conclusion that isomers of this type would appear as a resonance hybrid, here a non-polar or slightly polar double bond.

One is left, therefore, with the second alternative, that two products from the normal addition of halogen acids to ethylenic bonds are the result of the nearly identical activation energies of the two reactions, and that this would occur only when the two groups are about equal in electronegativity. This seems to be as far as one can go in the light of present-day experimental knowledge.

Summary

1. The addition of hydrogen chloride and hydrogen bromide to *cis*- and *trans*-2-pentene has been reinvestigated.

2. The ratio of products has been found to be independent of the conditions of addition and the isomer of 2-pentene employed.

3. The conditions under which two products are obtained upon normal addition of hydrogen halides to an ethylene bond and their theoretical implications are discussed.

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XX. The Addition of Hydrogen Bromide to 2-Butyne and 2-Bromo-2-butene

Since the report in 1933 of the reversal by certain catalysts, notably oxygen and organic peroxides, of the direction of addition of hydrogen bromide to olefins,² investigation in this Laboratory and elsewhere has disclosed some thirty olefins which undergo such a reversal of the direction of addition.³ In all of these, addition occurs to a terminal double bond, while with a number of other olefins with non-terminal double bonds, no such reversal has been observed. Accordingly, it has become of increasing interest to know whether the presence of a terminal double bond is essential for this phenomenon.

The addition of the second of two molecules of hydrogen bromide to 2-butyne⁴ appeared as a likely subject for investigation for two reasons. In the first place, the unsymmetrical distribution of substituents about the double bond in 2-bromo-2-butene would be expected to yield only one product of normal addition. Secondly, it has been observed in this Laboratory that halogen atoms attached to a molecule favor abnormal addition by retarding the normal reaction.

Addition of hydrogen bromide was carried out under the conditions specified in Table I, 5.4 g. of butyne being used in every instance. In the experiments marked "vacuum" the usual technique developed in this Laboratory was employed,² with evacuation to a pressure of 10^{-4} to 10^{-5} mm. After addition, the reaction mixture was first distilled at 5–10 mm. directly from the tubes in which the reaction took place into a trap at -80° , and the yield was determined at this point. In the case of additions in pentane the solvent was evaporated before distillation, while in experiments carried out in acetic acid the products were washed with water. All products were then distilled at 30 mm. in a Podbielniak column, and the index of the main fraction was taken. The first few drops of distillate and material which did not

distill were rejected, but loss by this method rarely exceeded 2 g.

Experimental Part

2-Butyne was prepared from sodium acetylide, sodamide, and dimethyl sulfate in liquid ammonia by the method of Bried and Hennion⁵ except that the reaction was carried out in a flask cooled in a bath of solid carbon dioxide and acetone. In this way the temperature of the reaction mixture was held at -70 to -60° during the addition of the dimethyl sulfate. The products were distilled through water to remove ammonia, and collected in a vessel cooled in ice water. Loss of product from the receiver was prevented by a trap maintained at -80° . With the use of a 2-liter flask containing about 1 liter of ammonia, 2 moles of sodium acetylide and other reagents in proportion could be handled with ease. The product was fractionated through a Podbielniak column. The yield from four moles of sodium acetylide was 88 g. (41%) of 2-butyne; b. p. $27.0-4^{\circ}$ (754 mm.); m. p. -28° to -27° ; n_D^{20} 1.3920.

Identification of Products.—Analysis was by index of refraction, checked by the boiling range of the products. The wide difference in index and boiling point of the two products makes the analyses certain to at least 5%. The most probable index of 2,2-dibromobutane was determined as n_D^{20} 1.5015 by measurements, after another fractionation, on the combined products of the experiments showing normal addition. The material was definitely identified by conversion to the 2,4-dinitrophenylhydrazone of methyl ethyl ketone (m. p. $111-112^{\circ}$; melting point of mixture with known sample $111-112^{\circ}$). The racemic 2,3-dibromobutane was identified by boiling point and index of refraction.

As the meso and racemic forms of 2,3-dibromobutane have different indices of refraction (n_D^{20} 1.5116 and 1.5147, respectively),⁶ the question naturally arises as to whether variations in the index of the abnormal products are due to variations in the ratios of the isomeric 2,3-dibromobutanes or to the presence of small quantities of 2,2-dibromobutane. To answer this question, the products of all experiments giving the abnormal product were combined and carefully fractionated through a Podbielniak column.⁷ While the first portion had an index of 1.5108, indicating it to be largely 2,2-dibromobutane, the remaining 80% had an index of 1.5145–7. Thus, the abnormal product appears to be entirely the racemic isomer, and the percentages of normal and abnormal product are calculated on this basis.

Discussion of Results

The results of the experiments are summarized in Table I. It will be noted that under most con-

(2) Kharasch and Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

(3) See Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937), for references to the subject.

(4) As the product of the addition of one molecule of hydrogen bromide to 2-butyne is necessarily 2-bromo-2-butene under all conditions, no necessity of isolating this intermediate arises. There is no reason to expect that the *cis* and *trans* isomers would give rise to different products (see ref. 7).

(5) Bried and Hennion, *J. Am. Chem. Soc.*, **59**, 1310 (1937).

(6) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

(7) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119 (1933).

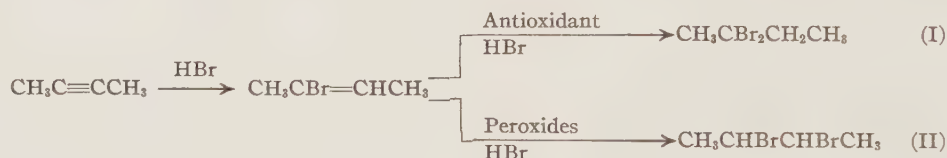
TABLE I
 ADDITION OF HYDROGEN BROMIDE TO 2-BUTYNE

Expt.	Mol. HBr ^a	Temp., °C.	Conditions of addition		Mol. ^a	Vacuum technique	Yield, %	B. p. (30 mm.) °C.	Product ^e	% 2,2-di bromide
			Time, hr.	Substance Added					<i>n</i> _D ²⁰	
III	2.4	20	2	Catechol	0.04	(+)	60 ^d	52	1.5022	95
V	2.0	20	12	Diphenylamine	.02	(+)	60 ^{b,d}	30-53	1.4947	(100)
VI	2.2	20	2	Diphenylamine	.02	(+)	65 ^d	51-52	1.5012	100
IV	3.0	-80	12	FeBr ₃	.01	(-)	50 ^d	51	1.5018	98
XI	2.4	20	22		...	(-)	75	51-53	1.5013	100
X	2.4	20	22	Acetic acid	2.0	(+)	85	51-53	1.5012	100
II	2.5	20	12	Acetic acid ^c	2.00	(-)	98	62	1.5139	6
VII	2.5	20	2	Acetic acid ^c	2.0	(-)	95	62-63	1.5132	11
VIII	2.6	20	5	Ascaridole	0.04	(-)	90	51-60	1.5022	95
I	2.6	20	24	Ascaridole	.03	(-)	100	52-64	1.5070	58
IX	2.4	20	4	Ascaridole	.04	(-)	85	62-65	1.5134	10
XII	2.5	20	12	Pentane	6.0	(-)	90	62-64.5	1.5142	4
				Ascaridole	.04					
				Pentane	6.0					

^a In moles per mole of 2-butyne. ^b Considerable 2-bromo-2-butene in product. ^c Sample of 2-butyne employed gave very strong test for peroxide. ^d Not including 10-20% of dark, non-volatile material obtained. ^e Indices used in analysis: 2,2-dibromobutane, *n*_D²⁰ 1.5015; racemic 2,3-dibromobutane *n*_D²⁰ 1.5147.

ditions described in Table I the product is exclusively normal, namely, 2,2-dibromobutane,⁸ and that even the addition of 3 mole per cent. of ascaridole fails to reverse the addition completely. However, when the normal addition is retarded by dilution with pentane, the product is almost exclusively abnormal. In acetic acid solution; addition is normal (expt. X) except when the 2-butyne has a high peroxide content (expts. II and VII).

and it cannot be determined whether or not reversal takes place. A border-line case is that of 2-bromopropene, which gives a 2:1 mixture on normal addition and a single product in the presence of oxygen or peroxides.³ (2) Compounds in which double bonds are conjugated with carboxyl and similar groups. (3) Compounds for which abnormal addition is masked by a very rapid normal reaction. All known cases of failure to obtain a reversal of the direction of addition of hy-



The discovery of a case of abnormal addition to a non-terminal double bond considerably increases the number of compounds which may be expected to undergo this reaction. In fact, it now seems likely that, with certain exceptions, abnormal addition to any ethylenic bond may be observed. The exceptions appear to be as follows. (1) Compounds in which symmetrical substitution by groups of the same order of electronegativity results in a double bond of low polarity. Compounds such as 2-pentene⁹ and 9-undecenoic acid¹⁰ give an equimolecular mixture of two addition products in the presence or absence of peroxides,

drogen bromide in the presence of peroxides seem to fall into one of these three classes.

The effect of a rapid normal addition in the abnormal reaction is clearly demonstrated in the case of 2-butyne. Here, the normal reaction is comparatively rapid (almost complete in two hours at 0°), with the result that only upon dilution does the abnormal reaction become important. The abnormal reaction, being presumably a chain reaction,³ is not retarded greatly by dilution with an inert solvent.

The principle of preferential retardation of the normal reaction by dilution appears to be a valuable tool, and it is now being employed in this Laboratory in attempts to detect abnormal addition in the addition of hydrogen bromide to several olefins which show a rapid normal reaction.

(8) This is the product reported by Wislicenus and Hölz, *Ann.*, **250**, 232 (1889).

(9) Kharasch, Walling and Mayo, *J. Am. Chem. Soc.*, **61**, 1559 (1939).

(10) Abraham, Mowat and Smith, *J. Chem. Soc.*, 948 (1937).

Summary

1. 2-Butyne adds hydrogen bromide in the absence of oxygen and peroxides to give 2,2-dibromobutane.

2. Under the influence of peroxide catalysis racemic 2,3-dibromobutane is obtained. This product is most easily obtained by retarding the normal reaction through dilution with an inert solvent.

The Peroxide Effect in the Addition of Reagents to Unsaturated Substances. XXII. The Addition of Hydrogen Bromide to Trimethylethylene, Styrene, Crotonic Acid, and Ethyl Crotonate

Recently an abnormal addition of hydrogen bromide to 2-bromo-2-butene was described under peroxidic conditions in dilute solution, and the efficacy of this method of obtaining the abnormal product was noted.² Further interesting results, with the aid of this technique, now have been obtained with several more olefins.

Addition of Hydrogen Bromide to Trimethylethylene.—In 1904 Ipatieff and Dechanov³ observed that, while treatment of trimethylethylene with hydrogen iodide or aqueous hydrobromic

acid yielded exclusively the tertiary halide, addition of hydrogen bromide in 60% acetic acid gave 10–25% of *s*-isoamyl bromide (2-methyl-3-bromobutane). A similar result was reported by Michael and Zeidler.⁴ Recently, however, Smith⁵ has indicated that *t*-amyl bromide is the sole product of the addition of hydrogen bromide to this olefin and that peroxides are without effect upon the course of the reaction, but unfortunately he does not describe the experimental conditions employed. The latter conclusion is contradicted by the results of this investigation, as shown in Table I. In the absence of a solvent and air and in the presence of an inhibitor, a

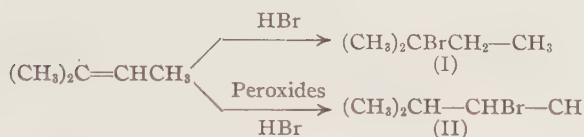
(2) Walling, Kharasch and Mayo, *J. Am. Chem. Soc.*, **61**, 1711 (1939).

(3) Ipatieff and Dechanov, *Chem. Zentr.*, **75**, II, 961 (1904).

(4) Michael and Zeidler, *Ann.*, **385**, 271 (1911).

(5) Smith, *Chemistry and Industry*, **57**, 561 (1938).

product containing 95% of the normal addition product, *t*-amyl bromide (I), results. Addition in pentane solution containing lauroyl peroxide yields as much as 64% of the abnormal addition product, 2-methyl-3-bromobutane (II). When the peroxide is replaced by diphenylamine, the product is chiefly normal, indicating that reversal is not due to the solvent itself.



Experiments in the presence of peroxides in ethyl bromide⁶ and nitrobenzene gave 60 and 100% of normal product, respectively. A similar if less pronounced difficulty in detecting abnormal addition in nitrobenzene solution has been

TABLE I
THE ADDITION OF HYDROGEN BROMIDE TO TRIMETHYLETHYLENE

Expt.	Substance added	Moles ^a	Yield, %	% <i>t</i> -Amyl bromide By index of refraction	By hydrolysis
VII	Diphenylamine ^b	0.02	73	100	95
IX	Hydroquinone ^b	0.03	83	94	93
III		...	68	70	71
XII		...	73	70	75
IV	Lauroyl peroxide	0.01	73	82	80
XVI	Lauroyl peroxide	0.01	81	76	74
VIII	Diphenylamine	0.02	66	79	77
	Pentane	6.0			
I	Lauroyl peroxide	0.05	70	52	40
	Pentane	10.00			
II	Lauroyl peroxide	0.05	66	40	36
	Pentane	10.00			
V	Pentane ^c	10.00	72	46	41
XI	Lauroyl peroxide	0.05	55	(109)	100
	Nitrobenzene	10.00			
XIV	Lauroyl peroxide	0.05	65	64	60
	Ethyl bromide	10.00			

^a In moles per mole of ethylene derivative. ^b Vacuum technique employed. ^c Reaction mixture illuminated with 500-watt incandescent lamp during addition.

observed in the addition of hydrogen bromide to isobutylene.⁷

A possible explanation of the failure of Smith to obtain evidence of abnormal addition to trimethylethylene lies in the ease with which the abnormal product undergoes isomerization. Thus, treatment of methylisopropylcarbinol or isopro-

(6) The result recorded in Table I was obtained with ethyl bromide purified by washing thoroughly with sulfuric acid, followed by fractionation. Two experiments with ordinary commercial ethyl bromide (which apparently contained alcohol or ether, as it darkened sulfuric acid) gave only the normal product, a result which seems reasonable in view of the ability of alcohol to inhibit reactions involving bromine atoms.

(7) Kharasch and Potts, *J. Am. Chem. Soc.*, **55**, 57 (1936).

pylene with hydrogen bromide yields, respectively, 79⁴ (p. 284) and 48%⁸ of the tertiary halide. In order to avoid this complication in the work reported here, any prolonged contact of the addition products with hydrogen bromide was avoided, and all distillations were carried out at reduced pressure.

Addition of Hydrogen Bromide to Styrene.—Although it is generally considered that the product obtained by adding hydrogen bromide to styrene is α -phenylethyl bromide, it has been observed that thiophenol,^{9,10} thioglycolic acid,¹¹ and bisulfite¹² all add abnormally to this olefin to yield β -phenylethyl derivatives. Also, a method has been described in the patent literature¹³ for treating styrene with hydrogen bromide at 95° in ethylbenzene solution in the presence of benzoyl peroxide. Under these conditions, it is claimed that the product contains 92% β -phenylethyl bromide.

TABLE II
THE ADDITION OF HYDROGEN BROMIDE TO STYRENE

Expt.	Substance added	Moles ^a	Yield, %	Product α -Phenylethyl bromide, %
V	Diphenylamine ^b	0.02	65	100
VII	Diphenylamine ^b	0.02	70	100
II		...	70	95
VIII		...	85	100
VI	Diphenylamine	0.02	65	95
	Pentane	6.00		
IX	Lauroyl peroxide	0.01	80	93
III	Ascaridole	0.05	70	45
	Pentane	10.00		
I	Ascaridole	0.05	60	42
	Pentane	7.0		
IV	Lauroyl peroxide	0.02	70	29
	Pentane	10.00		
X	Lauroyl peroxide ^c	0.02	75	20
	Pentane	6.0		

^{a,b} Have the same significance as in Table I. ^c Hydrogen bromide passed in during several hours.

Accordingly, it was of especial interest to investigate this problem. It has now been found that in absence of solvent styrene adds hydrogen bromide almost instantaneously to form α -phenylethyl bromide (III), and that even the presence of added peroxide does not lead to the formation of over 7% of the abnormal product (Table II).

(8) Michael and Leupold, *Ann.*, **379**, 296 (1911).

(9) Posner, *Ber.*, **38**, 646 (1905).

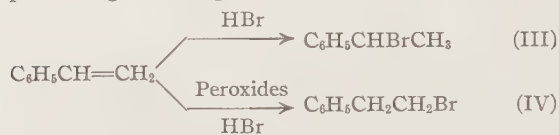
(10) Ashworth and Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(11) Holmberg, *J. prakt. Chem.*, **141**, 93 (1934); Kharasch, Read and Mayo, *Chemistry and Industry*, **57**, 752 (1938).

(12) Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938).

(13) Société des usines chimiques Rhône-Poulenc, British Patent 438,820 (1935); *C. A.*, **30**, 2993 (1936).

However, when the normal reaction is retarded by working in dilute pentane solution and peroxides are added, products may be isolated which contain as much as 80% of β -phenylethyl bromide (IV). There seems to be no reason to doubt that greater dilution and the slower addition of the halogen acid would result in an even greater percentage of this product.



Addition of Hydrogen Bromide to Crotonic Acid and Ethyl Crotonate.—Preliminary investigation in this Laboratory has found only one product (the usual β -bromo derivative) in the addition of hydrogen bromide to acrylic, crotonic and bromocrotonic acids¹⁴ in both the presence and absence of oxygen and peroxides. Furthermore, no reversal of addition has been obtained with bromomaleic,¹⁵ bromofumaric,¹⁵ and tetrolic acid,¹⁶ although in the latter case there is evidence that the products obtained in the presence of peroxides are stereoisomeric with those obtained in the absence of these materials.

It can now be said that even in the presence of a peroxide, illumination, and dilution with a solvent such as pentane, the only products of the addition of hydrogen bromide to crotonic acid and ethyl crotonate are the β -bromo derivatives.

Discussion

It is well established and is further shown in this paper that the normal addition of hydrogen bromide to olefins in which the double bond is not at the end of a hydrocarbon chain or is conjugated with a benzenoid nucleus proceeds with great rapidity. The present work shows that when these addition reactions are carried out in dilute pentane solution the normal reaction is retarded, and considerable abnormal addition of hydrogen bromide is observed. The previous paper in this series reached a similar conclusion in the case of 2-bromo-2-butene.

However, even though these conditions markedly retard the addition of hydrogen bromide to crotonic acid and its ethyl ester, no reversal of the direction of addition could be observed under even the most favorable conditions; neither do peroxides markedly accelerate the addition of hydro-

gen bromide to these substances in dilute pentane solution as they do in the case of other olefins.¹⁷ This fact may indicate that the chain mechanism postulated for abnormal addition¹⁸ is inoperative in the case of ethylenic bonds conjugated with a carboxyl or similar group. However, the alternative explanation cannot be excluded, that the mechanisms of both normal and abnormal addition lead, in the case of these compounds, to the formation of the same product. Indeed this explanation is to some extent supported by the reaction of tetrolic acids cited previously.

Experimental

Trimethylethylene and Hydrogen Bromide.—Trimethylethylene was prepared from Eastman *t*-amyl alcohol. Four hundred grams was placed in a distilling flask equipped with an efficient condenser and a "cold finger" in the neck of the flask to minimize the distillation of alcohol. Thirty cubic centimeters of concentrated sulfuric acid was added, and the flask heated on a steam-bath. Distillation of the product (together with a little alcohol and water) began almost at once, and the reaction was practically complete in two hours. The distillate was washed with sodium carbonate solution, dried over calcium chloride, and distilled through a 1.5-meter packed column. Two fractionations yielded 114 g. (36%) of trimethylethylene, b. p. 37.6–38.0° (744 mm.).

Addition of hydrogen bromide was carried out as indicated in Table I. Seven grams (0.1 mole) of trimethylethylene was used in all experiments. The pentane employed was a 30–35° fraction free from unsaturated material obtained from the Skelly Oil Company, Tulsa, Oklahoma. Hydrogen bromide was passed in (at room temperature except in vacuum experiments) and seemed to react as rapidly as it was added. After the removal of solvent the products were distilled at 100 mm. through a Podbielniak column. The yield recorded in the table is the amount of distillate collected at 47–52°. In the experiment in nitrobenzene the addition products were quickly distilled from the reaction mixture at reduced pressure and then fractionated.

Preliminary experiments on a redistilled sample of Kahlbaum *t*-amyl bromide, n_D^{20} 1.4420, indicated that it was hydrolyzed to the extent of 95% in fifteen minutes at 100° in 80% aqueous acetone, and that under the conditions of the experiment this amount presumably represented an equilibrium, as longer heating produced no fur-

(17) As an example, 0.1 mole of crotonic acid in 1.2 moles of pentane kept saturated with hydrogen bromide at about 20° reacted only to the extent of 40% in six hours, despite strong illumination and the presence of 0.0025 mole of lauroyl peroxide. In absence of solvent, crotonic acid, if warmed to start the reaction, will absorb the theoretical amount of hydrogen bromide in a few minutes. Propylene, by way of contrast, is subject to abnormal addition, and, while it undergoes the normal reaction in absence of solvent at a rate roughly comparable with crotonic acid, it reacts completely with hydrogen bromide in a few minutes in dilute pentane solution in the presence of only traces of peroxides (Mayo and Savoyias, kinetic investigation now in progress in this Laboratory).

(18) Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(14) Kharasch and McNab, unpublished work.

(15) Kharasch, Mansfield and Mayo, unpublished work.

(16) Grigorieff, Ph.D. Dissertation, University of Chicago, 1939.

ther hydrolysis. Similarly, when the products of experiments I, II, and V were combined and carefully fractionated into four portions, the third and fourth fractions (which presumably contained the greatest proportion of 2-methyl-3-bromobutane) were hydrolyzed by this procedure to the extent of 17.9 and 5.7%, respectively. As it seemed likely that even the highest boiling fraction contained some *t*-amyl bromide, it was assumed for purposes of calculation that 2-methyl-3-bromobutane was not measurably hydrolyzed under these conditions. Accordingly, 0.3 g. of the addition products was weighed out into Pyrex tubes of about 10 cc. capacity, and 5 cc. of 80% aqueous acetone added. The tubes were then sealed and placed in boiling water for fifteen minutes. After cooling and opening, the liberated acid was titrated with standard base.

As an additional check, the indices of refraction of all products were determined, and the percentage of normal and abnormal product calculated. Although results by both methods are included in Table I, I consider those obtained by hydrolysis to be the more accurate. The index of refraction of 2-methyl-3-bromobutane was found to be n_D^{20} 1.4453 by extrapolation.

Styrene and Hydrogen Bromide.—Styrene used in this investigation was obtained from the Bakelite Corporation, Bloomfield, New Jersey. As it contained hydroquinone to prevent polymerization, it was distilled *in vacuo* shortly before use. Experiments were performed as indicated in Table II. In all experiments, 10.4 g. of styrene was used; 9 g. of hydrogen bromide was passed in (at room temperature in all except vacuum experiments) and in no case did addition appear to require more than a few minutes. The products were worked up by distillation through a Podbielniak column at a pressure of 9 mm. of mercury. The yield recorded in Table II is based upon the weight of the fraction collected. In cases of addition in pentane, the solvent was removed before distillation by evaporation at atmospheric pressure.

For analysis, 0.2 g. of the product was weighed out into a Pyrex tube of about 10 cc. capacity, and 5 cc. of 80% aqueous acetone added. After sealing and heating for two hours in boiling water, the liberated acid was titrated with standard base. Experiments with samples of known composition indicated that, under these conditions, hydrolysis proceeded to the extent of 95% with α -phenylethyl bromide as compared with less than 2% with β -phenylethyl bromide.

As a further check, the addition product of experiment I (Table II) were treated with alcoholic potassium hydrosulfide,¹⁹ and the potassium salts of the resulting mercaptans allowed to react with 2,4-dinitrochlorobenzene according to the procedure of Bost, Turner, and Norton.²⁰ From the reaction mixture, β -phenylethyl 2,4-dinitrophenyl sulfide was obtained in yellow pearly plates (m. p. after crystallization from alcohol 87–88°). Similar treatment of the product from experiment II yielded α -phenylethyl 2,4-dinitrophenyl sulfide (orange crystals, m. p. after crystallization from alcohol 108–109°).

Addition to Crotonic Acid and Ethyl Crotonate.—Two sets of conditions were chosen as favoring the abnormal reaction. (a) One-tenth mole of crotonic acid or ethyl

crotonate, 0.0025 mole of lauroyl peroxide, and 1.0 to 1.2 moles of pentane were placed in a Pyrex bomb tube and cooled to -80° . One-eighth mole of hydrogen bromide was passed in, the tube sealed, and allowed to warm to room temperature. After standing overnight, the tubes were opened, the solvent evaporated off, and the products distilled under reduced pressure. (b) Hydrogen bromide (0.14–0.16 mole) was condensed in a Pyrex tube cooled to -80° . By carefully raising the tube from the cooling-bath, a very slow stream of hydrogen bromide could be obtained. This was bubbled very slowly through another Pyrex vessel containing 0.1 mole of the unsaturated material and 0.0025 mole of lauroyl peroxide in 1.2 moles of pentane. During the addition the vessel was illuminated by a 500-watt incandescent lamp at a distance of 15 cm. and cooled to about 20° by a stream of water. After three to six hours the product was worked up as described under (a). Under these conditions, crotonic acid added hydrogen bromide to the extent of 40% in six hours, while in the case of ethyl crotonate the reaction was virtually complete in three hours.

Fifteen-hundredths gram of the crotonic acid addition product was weighed into a flask, and 2.00 ml. of 1.942 *N* potassium hydroxide solution added. After standing for one hour at room temperature the mixture was diluted with water and titrated with standard acid. Under these conditions hydrogen bromide was liberated from known α - and β -bromobutyric acids to the extent of 3 and 98%, respectively. By this method all samples obtained by the addition of hydrogen bromide to crotonic acid contained over 95% of the β -bromo acid. A different method of analysis was used for the ester addition products on account of the partial hydrolysis of the esters. Three-tenths gram of the addition product was weighed out and 2.0 cc. of 1.8 *N* alcoholic potassium hydroxide added. After one minute the mixture was diluted with water and acidified with nitric acid. After addition of an excess of standard silver nitrate solution, the mixture was back titrated with ammonium thiocyanate solution. Under these conditions the α - and β -bromo esters liberated 1.3 and 99.3%, respectively, of the theoretical bromide ion. By this method, all samples obtained by addition of hydrogen bromide to ethyl crotonate contained 97% or more of ethyl β -bromobutyrate.

Summary

1. Trimethylethylene adds hydrogen bromide in the absence of oxygen and peroxides to give *t*-amyl bromide. Under conditions of peroxide catalysis the product contains as much as 64% of the abnormal product, 2-methyl-3-bromobutane.
2. Styrene adds hydrogen bromide in the absence of oxygen and peroxides to give α -phenylethyl bromide. Under conditions of peroxide catalysis and in the presence of solvent the product contains as much as 80% β -phenylethyl bromide.
3. In presence or absence of peroxides, crotonic acid and ethyl crotonate yield only β -bromobutyric acid and ethyl β -bromobutyrate, respectively.

(19) Sontag, *Ann. Chim.*, (11) 1, 428 (1934).

(20) Bost, Turner, and Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

